

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
25 November 2004 (25.11.2004)

PCT

(10) International Publication Number
WO 2004/100904 A1

- (51) International Patent Classification: **A61K 7/00**
- (21) International Application Number:
PCT/US2004/014336
- (22) International Filing Date: 7 May 2004 (07.05.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
60/468,439 7 May 2003 (07.05.2003) US
- (71) Applicant (for all designated States except US): **THE LUBRIZOL CORPORATION** [US/US]; 29400 Lakeland Blvd., Wickliffe, OH 44092-2298 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **FILIPPINI, Brian, B.** [US/US]; 5800 South Winds Drive, Apt. 132, Mentor-on-the-Lake, OH 44060 (US). **HUANG, Nai, Z.** [US/US]; 5488 Strathaven Drive, Highland Hts., OH 44143 (US). **CAREY, Jeffrey, M.** [US/US]; 6464 Dawson Blvd., Mentor, OH 44060 (US). **MULLAY, John, J.** [US/US]; 9251 Lori Jean Drive, Mentor, OH 44060 (US).
- (74) Agents: **GILBERT, Teresan, W.** et al.; The Lubrizol Corporation, Patent Dept./Mail Drop 022B, 29400 Lakeland Blvd., Wickliffe, OH 44092-2298 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**
- with international search report
 - before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: EMULSIFIERS FOR MULTIPLE EMULSIONS

(57) Abstract: The present invention relates to a stable multiple water-in-oil-in-water emulsion comprising: 1) an internal phase of a water-in-oil emulsion comprising a) a water discontinuous phase, b) an oil continuous phase, and c) a PIBSA emulsifier or derivative thereof; and 2) an external phase of an oil-in-water emulsion comprising: (a) an oil discontinuous phase comprising the internal phase water-in-oil emulsion; (b) an external water continuous phase; (c) an oil-in-water emulsifier; and (d) optionally water soluble thickeners; resulting in a stable water-in-oil in water multiple emulsion. The multiple emulsions are useful for personal care products.

WO 2004/100904 A1

TITLE: EMULSIFIERS FOR MULTIPLE EMULSIONS

This application claims priority from U.S. provisional application Serial
5 Number 60/468,439 filed May 7, 2003, now pending.

Field of the Invention

The present invention relates to a multiple emulsion, in particular a water-in-oil-in-water emulsion (WOW). The multiple emulsions are particularly useful in industrial, household and consumer products.

10 Additionally, the multiple emulsions are useful in personal care products.

Background of the Invention

The human need to look and feel satisfied with their personal appearance has provided growth to the personal care industry over the last several years. There are several different types of creams and lotions that
15 can be used that contain several different types of emulsified compositions in order to obtain the desired results.

A personal care product in the form of an emulsion may be made to the necessary and desired viscosity that is from a fluid to less fluid to a soft paste. An emulsified product has the further advantage of being pleasant in
20 appearance and easy to apply.

The majority of personal care products are in the form of emulsions that is water-in-oil (W/O) or oil-in-water (O/W), which allows the simultaneous use of lipophilic and hydrophilic ingredients in the required quantities. An emulsion is defined physically as a liquid system with two
25 fluids that are insoluble or only sparingly soluble in each other, and in which one phase is finely dispersed within the other. Personal care product emulsions generally consist of a polar water phase and a nonpolar oil phase and are either oil-in-water emulsions or water-in-oil emulsions. The necessary stabilization of the emulsion is achieved during production by the

introduction of an emulsifier which reduces the interfacial tension between the two phases. Emulsions are of great importance for personal care products, as they meet the physiological demands of the skin and permit uniform distribution of water soluble and oil soluble substances.

- 5 An obvious disadvantage in the use of emulsions is that the materials to be combined are not inherently compatible. The tendency is for the water and oil to separate.

 The problem is further magnified in the formulation of desired multiple emulsions that is water-in-oil-in-water ("WOW") or oil-in-water-in-oil ("OWO")
10 emulsions. Multiple WOW emulsions are systems formed from tiny drops of oil dispersed in water, but at the same time having even tinier drops of water encapsulated within the emulsified oil. In practical terms, a drop of oil contains other minute particles of water, and is suspended in water. In an emulsion of this type, there is a coexistence of a W/O emulsion in an O/W
15 emulsions. Naturally, it is possible to create the opposite; that is OWO emulsion system. Multiple emulsions allow the encapsulation, within the same product, of non-compatible active ingredients.

 Such multiple emulsions generally have not been practical because they tended to destabilize because of the presence of two incompatible
20 emulsifiers in one system. This instability is exacerbated in those cases in which either the middle oil phase or the external water phase has a relatively low viscosity. In these cases either greater coalescence can occur in the internal water-in-oil emulsion or greater settling or creaming can occur in the overall emulsion. This in turn leads to the need to add ingredients that
25 provide greater viscosity and also the use of large amounts of emulsifiers in order to maintain required stability properties. . However, large amounts of emulsifiers and/or consistency or viscosity modification factors can detract from the desired properties of the personal care product.

 Additionally, multiple emulsions have not been commercially useful
30 because the above mentioned emulsifier incompatibility causes the internal water-in-oil emulsion and the external oil-in-water emulsion to counteract each other and collapse to either a water-in-oil or an oil-in-water emulsion.

Thus, the multiple emulsions are destabilized and the product is rendered useless. It is desired to make a multiple emulsion so that the internal water-in-oil emulsion co-exists in the external aqueous phase for an acceptable period of time so as to make the overall product useful to consumers.

5 It is an object of this invention to provide a water-in-oil-in-water emulsion which is stable and has good emulsification properties and further can be commercially viable.

 It is an object of this invention to obtain a desired product with two incompatible active ingredients through a multiple emulsion that isolates the
10 active ingredients from each other and where the multiple emulsions is stable over time.

 It has been discovered that stable water-in-oil emulsions and multiple emulsions can be made with the emulsifiers of the present invention. Further it has been discovered that a stable multiple emulsion with two or
15 more incompatible active ingredients can be made.

Summary of the Invention

 The present invention relates to a stable multiple water-in-oil-in-water emulsion comprising:

- 20 1) A discontinuous phase, wherein that discontinuous phase is an internal water-in-oil emulsion comprising a) a water discontinuous phase, b) an oil continuous phase, c) either polyisobutenyl succinic anhydride-derived emulsifier(s) ("PIBSA") or polyisobutylene ("PIB") derived emulsifier(s) or both d) optionally a co-emulsifier and e) optionally thickeners for the discontinuous phase resulting in an internal water-in-oil emulsion; and
25 2) A continuous phase, wherein that continuous phase is an external aqueous phase comprising: a) water b) the internal water-in-oil emulsion, c) an oil-in-water emulsifier and c) optionally thickeners for the external aqueous phase

 resulting in a stable water-in-oil-in-water multiple emulsion.

30 The multiple emulsion of the present invention segregates non-compatible active ingredients and allows for stable coexistence of the

internal water-in-oil emulsion in the external aqueous phase. The multiple emulsion further provides good long-term storage properties.

The multiple emulsions are useful in industrial, household and consumer products. The multiple emulsions are useful in the personal care industry for dermatological, cosmetics, skin, hair, facial, sun care and the like type of products.

Detailed Description of the Invention

The present invention relates to stable multiple emulsions. The multiple emulsion is formed from the combination of an internal phase of a water-in-oil emulsion and an external aqueous phase.

The emulsifier includes PIBSA, PIB or PIBSA derivatives, functionalized PIB or PIBSA, and combinations thereof. In one embodiment the emulsifier is the reaction product of PIBSA with triethanolamine, in another embodiment the emulsifier is the reaction product of PIBSA with glycerol, and in another embodiment the emulsifier is the reaction product of PIBSA with sodium hydroxide.

PIBSAs are made by the reaction of poly(isobutylene) with maleic anhydride, providing the poly(isobutylene) succinic anhydride, or PIBSA. The PIBSA may contain about 30 to about 500 carbon atoms, and in one embodiment about 50 to about 300 carbon atoms, and in one embodiment about 60 to about 200 carbon atoms. In one embodiment, the hydrocarbyl substituents of these acylating agents have number average molecular weights of about 700 to about 10000, and in one embodiment about 900 to about 2300. Desirably the mole ratio of maleic anhydride to polyisobutylene present in the reaction mixture is less than 1.3:1 and in another embodiment is 1.3:1 to 2.5:1. More desirably the mole ratio is less than 1:1 and preferably is it from about 0.6:1 to about 0.9 or 1:1.

The emulsifier can then be made by reaction of the PIBSA with a nucleophile, such as an alcohol or polyol, an amine or polyamine, an amino alcohol, or a metal-containing base such as sodium hydroxide or potassium hydroxide.

In one embodiment, polyisobutenyl substituted phenols can be used as the PIB-derived emulsifier of this invention.

In another embodiment, functionalized polyisobutenyl phenols, such as amino polyisobutenyl phenols, can be used as the PIB-derived emulsifier of this experiment. These materials can be made by (a) the reaction of an alkylphenol directly with an aldehyde and an amine resulting in an alkylphenol connected by a methylene group to an amine or (b) the reaction of an alkylphenol with an aldehyde resulting in an oligomer wherein the alkylphenols are bridged with methylene groups, and the oligomer is then reacted with more aldehyde and an amine to give a Mannich product.

The reaction products of polyisobutylene with α,β -unsaturated olefins other than maleic anhydride can be further functionalized by reaction with nucleophiles like water, alcohol, polyols, amines, polyamines, alkanolamines, inorganic bases, etc., and these reaction products can also be used as emulsifiers for multiple emulsions as well. to be used as PIB-derived emulsifier in this invention in one embodiment.

The reaction products of polyisobutylene with glyoxylic acid, lower alkyl glyoxylates, such as methyl glyoxylate, or lower alkyl hemiacetals, such as acid methyl glyoxylate methyl hemiacetal, can be further functionalized with primary or secondary amines, primary or secondary alkanolamines, or polyamines, and these reaction products can also be used as the PIB-derived emulsifier in this invention.

In another embodiment, polyisobutenyl amine may be used as the PIB-derived emulsifier of this invention.

The emulsifier in the water-in-oil emulsion is used in the range from about 0.1 wt.% to about 30 wt.%, in another embodiment in the range from about 0.3 wt.% to about 10 wt.% and in another embodiment in the range from about 0.5 wt.% to about 8 wt.% of the final multiple emulsion.

The use of PIB or PIBSA and their derivatives as emulsifiers makes it possible to prepare water-in-oil emulsions that constitute stable resistant and tolerant emulsions that remain intact when blended into an external aqueous phase that contains an oil-in-water emulsifier.

The coemulsifier includes any emulsifier that will give a water-in-oil emulsion when used in combination with a PIB or PIBSA derived emulsifier. The two emulsifiers together should have a HLB value of 0-10 depending on the specific oil phase being used. The co-emulsifier includes sorbitan

5 monooleate, sorbitan monoisostearate, glycerol monooleate, oleyl alcohol 2-ethoxylate, lecithin, sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan sesquistearate, sorbitan trioleate, stearyl alcohol 2-ethoxylate, glycerol monostearate, sorbitan dioleate, refined wool fat, methyl glucoside dioleate, polyglyceryl-3 diisostearate, polyethylene glycol 200

10 distearate, methyl glucose sesquistearate, polyethylene glycol 200 monostearate and the like. In addition other alcohol alkoxylates as well as copolymers of various alkoxylates or ethoxylated amines and/or amides or betaines. Ionic surfactants can also be used in combination with the primary emulsifier described above as long as compatibility issues are not

15 encountered and that a water-in-oil emulsion is produced. The coemulsifier can be used alone or in combination.

However, any type of emulsifier meeting the HLB requirement can be used. Examples of other emulsifiers of this type can be found in McCutcheon's, Vol 1:Emulsifiers & Detergents, 2000, the contents which are

20 incorporated herein by reference.

The coemulsifier is present in the range from about 0 wt.% to about 10 wt.%, in one embodiment in the range from about 0.05 wt.% to about 8 wt.%, and in another embodiment in the range from about 0.2 wt.% to about 5 wt.% and of the internal water-in-oil emulsion

25 The aqueous phase may be any acceptable water based material and includes tap water, demineralized water, deionized water, floral water or the like. The water may be used alone or in combination.

The water is present in the range from about 1 wt.% to about 99 wt.%, in one embodiment in the range from about 20 wt.% to about 90

30 wt.% and in another embodiment in the range from about 20 wt.% to about 80 wt.% of the internal phase of the water-in-oil emulsion.

In the present case, the water and oil components and/or additives can be any of the standard components that are ordinary used for the desired emulsified product.

The oil phase includes all fatty substances conventionally used in the applications field, and in particular oils. The oils may be volatile or non-
5 volatile, or a mixture of both. The oils may be used alone or in combinations.

Suitable volatile oils include, both cyclic and linear silicones, such as octamethylcyclotetrasiloxane and decamethylcyclopentasiloxane; or straight or branched chain hydrocarbons having from 8-20 carbon atoms, such as
10 decane, dodecane, tridecane, tetradecane, squalane, hydrogenated polyisobutene, isohexadecane, or isoparaffins.

Non-volatile oils include, vegetable oils, such as apricot stone, avocado oil, macadamia nut oil, olive oil, coconut oil, jojoba oil, corn oil, sunflower oil, palm oil, soybean oil; carboxylic acid esters such as isostearyl
15 neopentanoate, cetyl octanoate, cetyl ricinoleate, octyl palmitate, dioctyl malate, coco-dicaprylate/caprate, decyl isostearate, myristyl myristate; animal oils such as lanolin, lanolin derivatives, tallow, mink oil, cholesterol; glyceryl esters, such as glyceryl stearate, glyceryl myristate; non-volatile silicones, such dimethicone, dimethiconol, dimethicone copolyol, phenyl
20 trimethicone, methicone, simethicone; nonvolatile hydrocarbons, such as isoparaffins, squalane; petroleum; mineral oils such as liquid paraffin; white oil, synthetic oils such as hydrogenated polyisobutene, esters of fatty acids and fatty alcohols (as C₆-C₃₀), ethers of fatty alcohols (as saturated and/or branched C₄-C₃₀ fatty alcohols); silicone oils, such as volatile cyclomethicone
25 oils, such as cyclotetradimethylsiloxane, cyclopentamethicone, cyclohexadimethylsiloxane or cyclohexamethicone; fluorinated oils; and mixtures thereof.

The oils include 2-ethylhexyl palmitate (or octyl palmitate), 2-ethylhexyl myristate (or octyl myristate), isopropyl palmitate, isopropyl
30 myristate, diisopropyl adipate, dioctyl adipate, 2-ethylhexyl hexanoate, ethyl laurate, methyl myristate, octyldodecyl octanoate, isodecyl neopentanoate, ethyl myristate, myristyl propionate, 2-ethylhexyl caprate/caprylate, methyl

palmitate, butyl myristate, isobutyl myristate, ethyl palmitate, isohexyl laurate, hexyl laurate, isopropyl isostearate, and mixtures thereof. The oils include fatty acid esters comprising at least 12 carbon atoms. In one embodiment these esters are obtained from a straight or branched amino
5 alcohol comprising from 1 to 17 carbon atoms and from a straight or branched chain fatty acid comprising at least 12 carbon atoms, preferably from 14 to 22 carbon atoms. In one embodiment the preferred oils are mono- or diesters.

In one embodiment, the oil of the emulsion contains (at least 50%) of
10 one or more hydrocarbon of oils comprising only carbon and hydrogen, which may be volatile or nonvolatile and may be mineral or synthetic. Suitable hydrocarbon oils include squalane, hydrogenated polyisobutene and hydrocarbon oils with a branched chain which preferably comprise from 6 to 20 and better still from 6 to 18 carbon atoms, for isohexadecane,
15 isododecane, isoparaffins and mixtures thereof.

In one embodiment for certain applications, the oil includes gasoline, diesel fuel, kerosene or the like.

The oil is present in the range from about 99 wt.% to about 1 wt.%, in another embodiment in the range from about 95 wt.% to about 5 wt.%, and
20 in another embodiment in the range from about 10 wt.% to about 30 wt.% of the internal phase of the water-in-oil emulsion.

One method for preparing the water-in-oil-in-water emulsion, involves adding the water-in-oil emulsion to an aqueous water phase which serves as the external phase of the multiple emulsions. In another embodiment, the
25 external aqueous phase may be added to the water-in-oil emulsion.

The external aqueous phase may be any acceptable water based material and includes tap water, demineralized water, deionized water, floral water or the like. The water may be used alone or in combination. The external water phase can be the same or different than the water used in the
30 aqueous phase of the water-in-oil emulsion.

The proportion of the aqueous phase in the internal water-in-oil emulsion to the external aqueous phase can be in the range of about 10 to

90:90 to 10, in another embodiment in the range of about 50 to 90:10 to 50 and in another embodiment in the range of about 20 to 40:60 to 80.

Added to the external aqueous phase, is a standard emulsifier having an HLB in the range of about 8 to about 20. The emulsifiers include

5 ethoxylates, nonionic ethoxylated fatty acids, esters, sorbitan esters, alkylphenols sorbitan monolaurate and the like. Other useful emulsifiers include carboxylates including amine salts, metallic salts and the like, alkylarylsulfonates, amine oxides, poly(oxyalkylene) compounds, including

10 block copolymers comprising alkylene oxide repeat units, carboxylated alcohol ethoxylates, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines and amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, fatty acid amides, including but not limited to amides from tall oil fatty acids and polyamides, ethoxylated glycerol esters, ethoxylated glycol esters, ethoxylated sorbitan esters, imidazoline

15 derivatives, lecithin and derivatives, lignin and derivatives, monoglycerides and derivatives, olefin sulfonates, phosphate esters and derivatives, propoxylated and ethoxylated fatty acids or alcohols or alkylphenols, sorbitan derivatives, sucrose esters and derivatives, sulfates or alcohols or ethoxylated alcohols or fatty esters, sulfonates of dodecyl and tridecyl

20 benzenes or condensed naphthalenes or petroleum, sulfosuccinates and derivatives, and tridecyl and dodecyl benzene sulfonic acids.

However, any type of emulsifier meeting the HLB requirement can be used. Examples of other emulsifiers of this type can be found in McCutcheon's, Vol 1:Emulsifiers & Detergents, 2000, the contents which are

25 incorporated herein by reference.

In one embodiment the emulsifier is Tween 20 (POE(20) sorbitan monolaurate) with an HLB of about 16.7, and Chemonix S-20 (a 20 ethoxylate stearyl alcohol with an HLB of about 15.0).

The emulsifiers may be used alone or in combination. The emulsifier

30 for the external aqueous phase is present in the range from about 0.01 wt.% to about 10 wt.%, in another embodiment the range from about 0.05 wt.% to

about 7 wt.% and in another embodiment in the range from about 0.1 wt.% to about 5 wt.% of the multiple emulsion.

The additives, depending on their nature, may be introduced into the oil phase, or into either of the aqueous phases or combinations thereof. The possible additional additives and/or their quantities are chosen so that the advantageous properties of the multiple emulsions are not or not substantially adversely affected by the addition of the additives.

The multiple emulsion can be thickened by using a thickener in the external aqueous phase, the internal aqueous phase, the oil phase or combinations thereof. If a thickener is used in any of the phases it can be the same or different or mixture thereof.

Thickeners for use in either aqueous phase include gums, such as xanthan gum, cellulose, chitosan, starches; silicates, magnesium aluminum silicates, hydroxyethylcellulose (such as the commercial product Natrosol cellulose or Cellosize), hydroxypropylcellulose (such as the commercial product Klucel), xanthan gums (such as the commercial product Rhodicare CFT from Rhodia) glucose-mannose polysaccharides, such as N-hance HP40 or N-hance HP40S, ammonium poly(acryldimethyltauramide-co-vinylformamide), also referred to as AMPS/VIFA copolymer, available commercially from Clariant Corporation, Charlotte, N.C. under the name trade name Aristoflex AVC; stearyl alcohol, cetyl alcohol, cetearyl alcohol, and various clays, such as hectorites, smectites and bentonites, including commercial products like Southern Clay Gel White MAS 100.

Thickeners for use in either aqueous phase further include crosslinked polyacrylic acid copolymer such as Carbopol® ETD 2020 available from Noveon, modified crosslinked polyacrylate polymer such as Carbopol® Ultrez available from Noveon, polyethoxylates of-methyl glucose and their derivatives, such as Glucamate LT available from (Chemron), PEG-120 methyl glucose dioleate, such as Glucamate™ DOE 120 available from (Chemron), starch, modified potato starch such as Structure® XL, Structure® ZEA available from National Starch and the like.

Thickeners for use in the oil phase include ethylene/ propylene/ styrene copolymers, butylene/ ethylene/styrene copolymers; commercial products like Versagel M750, Versagel ME 750, Versagel MP 500, Versagel MD 1600, available from Penreco; Transgel 105 and Transgel 110 available
5 from Rita; polyisobutylene, hydrogenated polyisobutylene, waxes, such as polyethylene wax, beeswax and the like; oil-soluble polyacrylates, oil soluble polymethacrylates, olefin polymers, olefin co-polymers, functionalized olefin copolymers, olefin terpolymers and functionalized olefin terpolymers, hydrophobically modified clays, silicas, and copolymers of styrene and
10 olefins.

The thickener may be used alone or in combination. The amount of thickener used will depend on the desired viscosity and/or desired stability of the multiple emulsion and is in the range from about 0 wt. % to about 10 wt.%, in another embodiment the range from about 0.1 wt.% of about
15 9 wt.%, and in another embodiment the range from about 1 wt.% from about 5 wt.% of the multiple emulsion.

The external aqueous phase, the aqueous phase in the internal emulsion or both phases may include water soluble additives, water dispersible additives and mixtures thereof. The water soluble additives may
20 be the same or different or combinations thereof in either the external or internal or both of the aqueous phases of the multiple emulsion. The water soluble additives may be used alone or in combination. The water dispersible additives may be the same or different or combinations thereof in either the external or internal or both of the aqueous phases of the multiple
25 emulsion. The water dispersible additives may be used alone or in combination.

Water soluble additives include solvents such as propylene glycol, active agents, preservatives, antioxidants, complexing agents, perfumes, fillers, bactericides, odor absorbers, color matter, dyes, lipid vesicles and the
30 like. Moisturizers such as protein hydrolysates and polyols such as glycerin; glycols such as polyethylene glycols; sugar derivatives; natural extracts; skin lightening agents, bleaching agents, botanicals, refatting agents, skin and

hair conditioners; vitamins, urea; caffeine; depigmenting agents such as kojic acid and caffeic acid; beta-hydroxy acids such as salicylic acid and its derivatives; alpha-hydroxy acids such as lactic acid and glycolic acid; emollients and humectants, such as ethoxylated methyl glucosides and acylated ethoxylated methyl glucosides; dihydroxyacetone, amino acids and mixture of amino acids, inorganic salts, inorganic oxides, sunscreens, retinoids such as retinol and its derivatives and carotenoids; organic and inorganic screening agents; hydrocortisone; DHEA; melatonin; algal, fungal, plant, yeast or bacterial extracts; proteins, hydrolysed, partially hydrolysed or unhydrolyzed; enzymes and mixtures thereof.

The water soluble additives can also include fertilizers, such as ammonium nitrate, urea, insecticides, fungicides, and bacteriocides.

The water soluble additives are in the range from about 0 % to about 30 %, and in another embodiment about 0.01 % to about 20 %, and in another embodiment from 0.1% to 5% and in another embodiment from .5 % to 3 % of the total weight of the multiple emulsions.

The water dispersible additives include clays, pigments, aluminum oxides, silicates, talc, magnesium silicates, titanium dioxide, and zinc oxide.

The water dispersible additives are in the range from about 0 % to about 30 %, in another embodiment about 0.01 % to about 20 % and in another embodiment about 0.5 % to about 10 % of the total weight of the multiple emulsions.

The oil phase includes any water immiscible additives acceptable in oil, such an oil being defined for the present purpose as any acceptable material which is substantially insoluble in water. As the oils can perform different functions in the composition, the specific choice is dependent on the purpose for which it is intended.

The oil phase includes lipophilic additives, fatty acids, fatty alcohols, gums, waxes, silicone gums, oily gelling agents, organic particles, inorganic particles and the like. The oil phase additives may be used alone or in combination.

The oil phase additives include the oil thickeners listed above; vitamins; organic sunblocks, such as avobenzone, octocrylene, cinnamate esters, salicylate esters; refatting agents; skin and hair conditioners; emollients and moisturizers; lanolins and any other additives that add to the performance of the emulsion in the intended end-use application.

The oil phase additives are in the range from about 0 wt.% to about 30 wt.%, in another embodiment in the range from about 0.1 wt.% to about 10 wt.%, in another embodiment in the range from about 1 wt.% to about 5 wt.% of the internal phase of the water-in-oil emulsion.

The multiple emulsions are conveniently but not necessarily prepared as conventional multiple emulsions are prepared. Initially, a water-in-oil emulsion is prepared according to standard procedure. Generally the water soluble ingredients are combined together in an aqueous vehicle, the oil soluble ingredients are combined in the oil vehicle, and the two phases are combined with the PIB and/or PIBSA emulsifier to form the water-in-oil emulsion. The water, the oil, the PIB and/or PIBSA emulsifier and desired additives are combined with stirring, shearing and combinations thereof, at a temperature in the range from ambient temperature to about 80°C. The water-in-oil emulsion is then incorporated into the external aqueous phase with emulsifiers and desired additives with mixing at a temperature in the range from about ambient temperature to about 65°C. The resulting emulsion is stable and intact as a multiple emulsion.

The water phase of the internal water-in-oil emulsion is comprised of droplets having a mean diameter of about 0.1 to about 5 microns, in one embodiment about 0.5 to about 3 microns or less, in another embodiment about 2 microns or less, in another embodiment about 1 micron or less. The internal water-in-oil emulsion in the external aqueous phase is comprised of droplets of the internal water-in-oil emulsion having a mean diameter of about 1 to about 50 microns, in another embodiment about 30 microns or less, in another embodiment about 10 microns or less, in another embodiment about 5 microns or more, in another embodiment about 10 micron to about 5 microns.

The multiple emulsions of the present invention provide a number of advantages over traditional multiple emulsions. The system permits for a greater concentration of the internal emulsion in the multiple emulsion, thereby permitting a broader variety of textures, and a broader appeal to a wide range of products. The multiple emulsions can be used to deliver a number of different types of active materials, partitioned among the various phases of the final product. This can be particularly important in a system in which there are several actives that may not be compatible together, or that may not exhibit optimum activity in the same environment. The multiple emulsion is stable.

The emulsions can essentially be used for any type of application in which an emulsion is used in particular for industrial, household and consumer products. Applications areas include metal working, horticulture, agriculture, coatings/ paints/ inks, lubricants and fuels. The multiple emulsion of this invention finds particular application in a large number of personal care applications, such as the treatment of, the protection of, and the care of skin, lip and nail, make-up removal and/or for cleansing the skin, and personal care products, such as sunscreens/self-tanners, rinse-off hair conditioners, liquid make ups and the like.

The invention will be further illustrated by the following non-limiting examples.

Specific Embodiment

Example 1: The oil phase of the primary emulsion includes white oil (about 15.7 g) as the oil, and Chemccinate 2000 (about 6.3g) [low color PIBSA/triethanolamine (1:1)m from Chemron] as the emulsifier. Dihydroxyacetone (DHA) (about 10.0g) is the tanning active ingredient and it is combined with about 66.95 g of water and 1.05 g of sodium chloride to prepare the aqueous phase of the primary emulsion. Both phases are heated to about 70°C, and the aqueous phase is added dropwise to the oil phase over about 20 minutes while mixing with a Heidolph mixer at about 600 rpm. Once the addition is complete, the water-in-oil emulsion is

homogenized at about 7000 rpm for about 10 minutes. The resulting emulsion is the internal water-in-oil emulsion of the multiple emulsion. The droplet size is in the about 0.5-2 micron range for the primary water-in-oil emulsion.

5 The external aqueous phase is prepared by combining the following ingredients at 50C with stirring: water (about 26.05g), preservative (about 0.2g), sodium chloride (about 0.28g), Chemonics S-20 (stearyl alcohol 20 ethoxylate) (about 3.0g), smectite clay (about 1.33g), and an amino acid complex (about 1.0g). The internal water-in-oil emulsion (about 66.8g) is
10 then added to the external aqueous phase over about 20 minutes at about 500 rpm. To this multiple emulsion is added a mixture of xanthan gum (about 0.67g) and 2-ethylhexyl stearate (about 0.67g) and the mixture is stirred for an additional about 30 minutes, followed by addition of a preservative.

15 This emulsion has shown excellent stability after 5 freeze thaw cycles (about -18C to ambient temperature) and about 43°C storage (two weeks) based on visual inspection, microscopy, and viscosity.

Example 2: The oil phase of the primary emulsion includes octyl stearate (about 15.7 g) as the oil, Chemccinate 2000 (about 6.3g) [low color
20 PIBSA/triethanolamine (1:1)m from Chemron] as the emulsifier. Dihydroxyacetone (DHA) (about 10.0g) is the tanning active ingredient and it is combined with about 66.95 g of water and about 1.05 g of sodium chloride to prepare the aqueous phase of the primary emulsion. Both phases are heated to about 70°C, and the aqueous phase is added dropwise to the oil
25 phase over about 20 minutes while mixing with a Heidolph mixer at about 600 rpm. Once the addition is complete, the water-in-oil emulsion is homogenized at about 7000 rpm for about 10 minutes. The resulting emulsion is the internal water-in-oil emulsion of the multiple emulsion. The droplet size is in the about 0.5-2 micron range for the primary water-in-oil
30 emulsion.

The external aqueous phase is prepared by combining the following ingredients at about 50°C with stirring: water (about 26.05g), preservative (about 0.2g), sodium chloride (about 0.28g), Chemonics S-20 (stearyl alcohol 20 ethoxylate) (about 3.0g), smectite clay (about 1.33g), and an amino acid complex (about 1.0g). The internal water-in-oil emulsion (about 66.8g) is then added to the external aqueous phase over about 20 minutes at about 500 rpm. To this multiple emulsion is added a mixture of xanthan gum (about 0.67g) and 2-ethylhexyl stearate (about 0.67g) and the mixture is stirred for an additional about 30 minutes, followed by addition of a preservative.

This emulsion has shown very good stability after 5 freeze thaw cycles (about -18°C to ambient temperature) and about 43°C storage (two weeks) based on visual inspection, microscopy, and viscosity.

Example 3: The oil phase of the primary emulsion is prepared by combining white oil (about 14.5 g), petrolatum (about 0.5g), Chemccinate 2000 (about 7.5g) [low color PIBSA/triethanolamine (1:1)m from Chemron] and sorbitan monoisostearate (about 1.5g). The aqueous phase is prepared by combining dihydroxyacetone (DHA) (about 10.0g), about 63.0 g of water and about 2.0 g of a smectite clay, about 0.5g of xanthan gum and about 0.5g of white oil. Both phases are heated to about 70°C, and the aqueous phase is added dropwise to the oil phase over about 20 minutes while mixing with a Heidolph mixer at about 600 rpm. Once the addition is complete, the water-in-oil emulsion is homogenized at about 7000 rpm for about 10 minutes. The resulting emulsion is the internal water-in-oil emulsion of the multiple emulsion. The droplet size is in the about 0.5-2 micron range for the primary water-in-oil emulsion.

The external aqueous phase is prepared by combining the following ingredients at about 50°C with stirring: water (about 34.2g), Chemonics S-20 (stearyl alcohol 20 ethoxylate) (about 3.0g), smectite clay (about 1.4g), and an amino acid complex (about 1.0g). The internal water-in-oil emulsion (about 60.0g) is then added to the external aqueous phase over about

20 minutes at about 500 rpm. To this multiple emulsion is added a mixture of xanthan gum (about 0.1g) and white oil (about 0.1g) and the mixture is stirred for an about additional about 30 minutes, followed by addition of a preservative (about 0.2g).

- 5 This emulsion has shown excellent stability after 5 freeze thaw cycles (about -18°C to ambient temperature) and about 43°C storage (two weeks) based on visual inspection, microscopy, and viscosity.

Example 4: The oil phase of the primary emulsion is prepared by combining white oil (about 15.7 g), Chemccinate 2000 (about 6.3g) [low color
10 PIBSA/triethanolamine (1:1)m from Chemron]. The aqueous phase is prepared by combining dihydroxyacetone (DHA) (about 10.0g), sodium chloride (about 1.0g), about 65.0 g of water and about 2.0 g of a smectite clay. Both phases are heated to about 70°C, and the aqueous phase is ,
added dropwise to the oil phase over about 20 minutes while mixing with a
15 Heidolph mixer at about 600 rpm. Once the addition is complete, the water-in-oil emulsion is homogenized at about 7000 rpm for about 10 minutes. The resulting emulsion is the internal water-in-oil emulsion of the multiple emulsion. The droplet size is in the about 0.5-2 micron range for the primary water-in-oil emulsion.

- 20 The external aqueous phase is prepared by combining the following ingredients at about 50°C with stirring: water (about 25.12g), sodium chloride (about 0.28g), Chemonix S-20 (stearyl alcohol 20 ethoxylate) (about 3.0g), smectite clay about 2.8g, and an amino acid complex (about 1.0g). The internal water-in-oil emulsion (about 66.6g) is then added to the external
25 aqueous phase over about 20 minutes at about 500 rpm. To this multiple emulsion is added a mixture of xanthan gum (about 0.5g) and white oil (about 0.5g) and the mixture is stirred for an additional about 30 minutes, followed by addition of a preservative (about 0.2g).

- 30 This emulsion has shown excellent stability after 5 freeze thaw cycles (about -18°C to ambient temperature) and about 43°C storage (two weeks) based on visual inspection, microscopy, and viscosity.

We claim

1. A multiple water-in-oil-in-water emulsion composition comprising:

- 5 (1) a discontinuous phase, wherein that discontinuous phase comprises a) a water discontinuous phase, b) an oil continuous phase, c) an emulsifier selected from the group consisting of a polyisobutenyl succinic anhydride-derived emulsifier(s), a polyisobutene derived emulsifier(s) and mixtures thereof, d) optionally a co-emulsifier and e) optionally thickeners for
- 10 the discontinuous phase resulting in an internal water-in-oil emulsion; and
- (2) a continuous phase, wherein that continuous phase is an external aqueous phase comprising a) water b) the internal water-in-oil emulsion, c) an oil-in-water emulsifier and c) optionally thickeners for the external aqueous phase;
- 15 resulting in a stable water-in-oil-in-water multiple emulsion.2

2. The composition of claim 1 wherein the polyisobutenyl succinic anhydride-derived emulsifier comprises the reaction product of poly(isobutylene) with maleic anhydride, poly(isobutylene) succinic anhydride, poly(isobutylene) succinic anhydride derivatives, functionalized
- 20 poly(isobutylene) succinic anhydride, the reaction product of poly(isobutylene) succinic anhydride with alcohol, amines, polyols, polyamines, and alkanolamines, the reaction product of poly(isobutylene) succinic anhydride with triethanolamine, the reaction product of poly(isobutylene) succinic anhydride with glycerol, the reaction product of
- 25 poly(isobutylene) succinic anhydride with sodium hydroxide, or combinations thereof.

3. The composition of claim 1 wherein the polyisobutylene derived emulsifier comprises polyisobutenyl substituted phenols, amino polyisobutenyl phenols, polyisobutenyl amine and mixtures thereof.

4. The composition of claim 1 wherein the polyisobutylene derived emulsifier comprises the reaction products of polyisobutylene with α,β -unsaturated olefins followed by further functionalized by reaction with nucleophiles like water, alcohol, polyols, amines, polyamines, alkanolamines, and inorganic bases.

5. The composition of claim 1 wherein the polyisobutylene derived emulsifier comprises the reaction products of polyisobutylene with glyoxylic acid, lower alkyl glyoxylates, such as methyl glyoxylate, or lower alkyl hemiacetals, such acid methyl glyoxylate methyl hemiacetal, followed by further functionalized with primary or secondary amines, primary or secondary alkanolamines, or polyamines.

6. The compositions of claim 1 wherein the emulsifier is used in the range of about 0.1 wt.% to about 30 wt.% of the final multiple emulsion.

7. The composition of claim 1 wherein the coemulsifier comprises sorbitan monooleate, sorbitan monoisostearate, glycerol monooleate, oleyl alcohol 2-ethoxylate, lecithin, sorbitan monolaurate, sorbitan monopalmitate, sorbitan monostearate, sorbitan sesquisterate, sorbitan trioleate, stearyl alcohol 2-ethoxylate, glycerol monostearate, sorbitan dioleate, wool fat, methyl glucoside dioleate, polyglyceryl-3 diisostearate, polyethylene glycol 200 distearate, methyl glucose sesquisterate, polyethylene glycol 200 monostearate, alcohol alkoxylates, copolymers of various alkoxylates, alkyl amines or alcohols or amides, ethoxylated alkyl amines or amides, betaines, compatible sulfonates or sulfates or sulfosuccinates or phosphonates or borates or amine salts or carboxylates, or mixtures thereof and the coemulsifier is present in the range from about 0 wt.% to about 10 wt.% of the internal water-in-oil emulsion.

8. The composition of claim 1 wherein the aqueous material comprises tap water, demineralized water, deionized water, floral water or

combinations thereof and the water is present in the range of about 1 wt.% to about 99 wt.% of the internal phase of the water emulsion.

9. The composition of claim 1 wherein the oil comprises fatty substances, volatile oils, non-volatile oils or mixtures thereof and the oil is
5 present in the range of about 99 wt.% to about 1 wt.% of the water-in-oil emulsion.

10. The composition of claim 1 wherein the external aqueous phase comprises tap water, demineralized water, deionized water, floral water or combinations thereof and wherein the internal water-in-oil emulsion to the
10 external aqueous phase is in the range of about 10 to 90:90 to 10.

11. The composition of claim 1 wherein the external aqueous phase emulsifier comprises ethoxylates, nonionic ethoxylated fatty acids, esters, sorbitan esters, alkylphenols sorbitan monolaurate, carboxylates, amine salts, metallic salts, alkylarylsulfonates, amine oxides, poly(oxyalkylene)
15 compounds, including block copolymers comprising alkylene oxide repeat units, carboxylated alcohol ethoxylates, ethoxylated alcohols, ethoxylated alkylphenols, ethoxylated amines and amides, ethoxylated fatty acids, ethoxylated fatty esters and oils, fatty esters, fatty acid amides, including but not limited to amides from tall oil fatty acids and polyamides, ethoxylated
20 glycerol esters, ethoxylated glycol esters, ethoxylated sorbitan esters, imidazoline derivatives, lecithin and derivatives, lignin and derivatives, monoglycerides and derivatives, olefin sulfonates, phosphate esters and derivatives, propoxylated and ethoxylated fatty acids or alcohols or alkylphenols, sorbitan derivatives, sucrose esters and derivatives, sulfates or
25 alcohols or ethoxylated alcohols or fatty esters, sulfonates of dodecyl and tridecyl benzenes or condensed naphthalenes or petroleum, sulfosuccinates and derivatives, and tridecyl and dodecyl benzene sulfonic acids or mixtures thereof and is present in the range from about 0.01 wt.% to about 10 wt.% of the multiple emulsion.

12. The composition of claim 1 wherein the multiple emulsion is thickened by a thickener comprising xanthan gum, cellulose, chitosan, starches, silicates, magnesium aluminum silicates, hydroxyethylcellulose, xanthan gums, glucose-mannose polysaccharides, ammonium

5 poly(acryldimethyltauramide-co-vinylformate), stearyl alcohol, cetyl alcohol, cetearyl alcohol, clays, hectorites, smectites, bentonites, crosslinked polyacrylic acid copolymer, modified crosslinked polyacrylate polymer, polyethoxylates of methyl glucose and their derivatives, PEG-120 methyl glucose dioleate, starch, modified potato starch, ethylene/propylene/styrene

10 copolymers, butylenes/ethylene/styrene copolymers, polyisobutylene, hydrogenated polyisobutylene, waxes, polyethylene wax, beeswax, oil soluble polyacrylates, oil soluble polymethacrylates, olefin polymers, olefin co-polymers, functionalized olefin copolymers, olefin terpolymers, functionalized olefin terpolymers, hydrophobically modified clays, silicas, and

15 copolymers of styrene and olefins or the mixtures thereof and wherein the thickener is in the range from about 0 wt.% to about 10 wt.% of the multiple emulsion.

13. The composition of claim 1 wherein the composition comprises water soluble additives comprising propylene glycol, active agents,

20 preservatives, antioxidants, complexing agents, perfumes, fillers, bactericides, odor absorbers, color matter, dyes, lipid vesicles, protein hydrolysates and polyols such as glycerin; glycols such as polyethylene glycols; sugar derivatives; natural extracts; skin lightening agents, bleaching agents, botanicals, refatting agents, skin and hair conditioners; vitamins,

25 urea; caffeine; depigmenting agents such as kojic acid and caffeic acid; beta-hydroxy acids such as salicylic acid and its derivatives; alpha-hydroxy acids such as lactic acid and glycolic acid; emollients and humectants, such as ethoxylated methyl glucosides and acylated ethoxylated methyl glucosides; dihydroxyacetone, amino acids and mixture of amino acids,

30 inorganic salts, inorganic oxides, sunscreens, retinoids such as retinol and its derivatives and carotenoids; organic and inorganic screening agents;

hydrocortisone; DHEA; melatonin; algal, fungal, plant, yeast or bacterial extracts; proteins, hydrolysed, partially hydrolysed or unhydrolyzed; enzymes or mixtures thereof and wherein the water soluble additives are in the range from about 0 wt.% to about 30% of the multiple emulsion.

5 14. The composition of claim 1 wherein the composition comprises water dispersable additives comprising clays, pigments, aluminum oxides, silicates, talc, magnesium silicates, titanium dioxide, zinc oxide or mixtures thereof and wherein the water dispersable additives are in the range from about 0 wt.% to about 30 wt.% of the multiple emulsion.

10 15. The composition of claim 1 wherein the oil composition comprises oil phase additives comprising lipophilic additives, fatty acids, fatty alcohols, gums, waxes, silicone gums, oil gelling agents, organic particles, inorganic particles, thickeners, vitamins, organic sunblocks, avobenzone, octocrylene, cinnamate esters, salicylate esters, refatting
15 agents, skin conditioners, hair conditioners, emollients, moisturizers, lanolins or mixtures thereof and wherein the oil phase additives are in the range from about 0 wt.% to 30 wt.% of the internal phase of the water-in-oil emulsion.

 16. The composition of claim 1 wherein the water phase of the internal water-in-oil emulsion is comprised of droplets having a mean
20 diameter of about 0.1 to about 5 microns.

 17. The composition of claim 1 wherein the internal water-in-oil emulsion in the external aqueous phase is comprised of droplets of the internal water-in-oil emulsion having a mean diameter of about 1 to about 50 microns.

25 18. The composition of claim 1 wherein the oil-in-water emulsifier has an HLB of about 8 to about 20.

 19. The composition of claim 1 used as multiple emulsion for products selected from the group consisting of industrial products, household

products, consumer products, personal care products, metal working products, horticulture products, agriculture products, coating products, paint products, ink products, lubricant products, fuel products and combinations thereof.

- 5 20. A method of making a multiple emulsion composition comprising combining an aqueous component in the range of about 1 wt.% to about 99 wt.% and an oil phase in the range of about 99 wt.% to 1 wt.% with an emulsifier selected from the group consisting of poly(isobutylentyl) succinic anhydride-derived emulsifier, a polyisobutylene derived emulsifier and
- 10 mixtures thereof to produce an internal water-in-oil emulsion, and then combining the internal water-in-oil in an external aqueous phase at a ratio of 10 to 90:90 to 10 with an emulsifier with a HLB of 8 to 20 resulting in a stable multiple emulsion.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2004/014336

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 A61K7/00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 A61K		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 717 978 A (CURTIS HELENE IND INC) 26 June 1996 (1996-06-26) page 3, line 39 - page 5, line 46 page 13, line 49 - line 59	1-20
A	EP 0 715 842 A (CURTIS HELENE IND INC) 12 June 1996 (1996-06-12) page 2, line 5 - page 7, line 3	1-20
Y	US 5 457 835 A (MANZO GIOVANNI) 17 October 1995 (1995-10-17) column 2, line 1 - line 51	1-20
Y	US 4 256 605 A (BAKER ALAN S) 17 March 1981 (1981-03-17) the whole document	1-20
----- -/--		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex		
<div style="display: flex; justify-content: space-between;"> <div style="width: 48%;"> <p>* Special categories of cited documents</p> <p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 48%;"> <p>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>*X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>*Y* document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>*&* document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-weight: bold;">22 October 2004</div>		Date of mailing of the international search report <div style="text-align: center; font-weight: bold;">02/11/2004</div>
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-weight: bold;">Irwin, L</div>

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/014336

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
Y	US 5 034 071 A (VANOMMEREN CATHARINE) 23 July 1991 (1991-07-23) column 3, line 15 - line 20 -----	1-20

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/014336

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0717978	A	26-06-1996	US 5589177 A	31-12-1996
			AU 709525 B2	02-09-1999
			AU 4026395 A	13-06-1996
			AU 688632 B2	12-03-1998
			AU 4027195 A	13-06-1996
			CA 2163854 A1	07-06-1996
			CN 1138982 A	01-01-1997
			EP 0717978 A2	26-06-1996
			FI 955866 A	07-06-1996
			NO 954916 A	07-06-1996
			NZ 280599 A	27-07-1997
			US 6022547 A	08-02-2000
			ZA 9510058 A	04-06-1996
EP 0715842	A	12-06-1996	US 5656280 A	12-08-1997
			CA 2161762 A1	07-06-1996
			CN 1131014 A	18-09-1996
			EP 0715842 A2	12-06-1996
			FI 955865 A	07-06-1996
			NO 954915 A	07-06-1996
			NZ 280600 A	27-07-1997
			US 5942216 A	24-08-1999
			ZA 9510064 A	05-06-1996
US 5457835	A	17-10-1995	AR 242993 A1	30-06-1993
			CA 1332661 C	25-10-1994
			DE 68910539 D1	16-12-1993
			DE 68910539 T2	24-02-1994
			EP 0324536 A1	19-07-1989
			ES 2048277 T3	16-03-1994
			JP 1308500 A	13-12-1989
			KR 155544 B1	16-11-1998
			MX 170021 B	04-08-1993
			TR 25221 A	26-11-1992
			YU 2589 A1	31-12-1990
US 4256605	A	17-03-1981	AU 520728 B2	25-02-1982
			AU 4523379 A	27-09-1979
			CA 1126123 A1	22-06-1982
			DE 2963798 D1	11-11-1982
			DK 111879 A	24-09-1979
			EP 0004426 A2	03-10-1979
			GB 2017719 A ,B	10-10-1979
			IT 1114216 B	27-01-1986
			JP 1508144 C	26-07-1989
			JP 54132492 A	15-10-1979
			JP 63051734 B	14-10-1988
			NZ 189911 A	14-11-1980
			ZA 7901170 A	26-03-1980
US 5034071	A	23-07-1991	AU 647131 B2	17-03-1994
			AU 7838591 A	19-12-1991
			CA 2042626 A1	15-12-1991
			MW 1391 A1	13-05-1992
			ZA 9103784 A	26-02-1992
			ZM 2091 A1	30-06-1992

THIS PAGE BLANK (USPTO)